Characterization of HVAC Filter Cake Composition and Ozone-initiated Heterogeneous Chemistry

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SUMMARY
The major goals of this study were to identify key organic constituents of particles deposited on heating ventilation and air conditioning (HVAC) filters and better understand the chemical mechanisms that contribute to negative impacts of building filtration systems on indoor air quality. Several types of filter media were investigated: fiberglass, polyester and cotton/polyester blend, each as unused and loaded for 3 months at two locations in the San Francisco Bay Area (California). Extracts of used filters were analyzed by gas chromatography-ion trap tandem mass spectroscopy. Among other compounds, the extracts contained terpene alcohols and their reaction byproducts, amides, phthalates and aromatic hydrocarbons. Sources of these compounds and their precursors include vegetation, occupant activities, emissions from indoor materials and urban pollution. To investigate heterogeneous reactions that could occur in ventilation systems, clean and used filters were mounted in a Teflon plug-flow reactor and spiked with a model pollutant (α-terpineol) before exposure to ozone (~150 ppb). Reaction products were identified downstream. Aerosol number size distribution was also monitored over the particle size range of 10 to 400 nm. Under some conditions, ozone reactions on the filters or with gas phase products generated ultrafine particles.

IMPLICATIONS
Ozone from outdoor air can react with compounds present on the surfaces of HVAC filters to form pollutants associated with asthma and building related symptoms (BRS).

KEY WORDS
HVAC filters, ozone, α-terpineol, terpenoids, filter cake

INTRODUCTION
Many commercial buildings use heating ventilation and air conditioning (HVAC) systems fitted with filters to remove airborne particles from indoor air. The main purpose of the ventilation system is to ensure good air quality by providing fresh outdoor air that dilutes indoor-generated pollutants. However, a number of studies (Fanger et al., 1988; Finke and Fitzner, 1993) have shown that such filters are associated with low perceived air quality.

The complex mixture of organic and inorganic compounds deposited on the surface of used filters ("filter cake") is often associated with low perceived air quality (Hyttinen et al., 2003). In addition to breakthrough of pollutants into supply air, filter cake can also act as a surface for sorption of semivolatile organic compounds (SVOCs) that can react with atmospheric oxidants such as ozone (Zhao et al, 2007) and other pollutants already present in filters, thereby forming ultrafine particulate matter and volatile byproducts. Filter cake also serves as a medium for the growth of bacteria and fungi that may also contribute to poor IAQ (Noris et al, 2009). One common SVOC measured in indoor air is 1-methyl-4-isopropyl-1-cyclohexen-8-ol (α-terpineol), which is a component of household product emissions (Destaillats et al, 2006). Ham and Wells (2008) have studied the ozone reactions of α-terpineol on vinyl and glass surfaces, and found that the surface reaction mechanism is different from gas phase chemistry. The nature of the surface (e.g., different porosity and rugged morphology) was seen to affect the reaction rates and type of byproducts formed. HVAC filters, having high surface area, can act as a substrate for surface reactions with ozone present in supply air. This study focuses on identifying organics condensed on filter cake from filters deployed in two locations in the San Francisco Bay Area that may be associated with BRS. Ozone reaction with α-terpineol spiked on filter surfaces is studied as a model system to understand these heterogeneous chemical processes.

MATERIALS AND METHODS

Characterization of filter cake: Three different types of HVAC filter samples were deployed and retrieved from the Port of Oakland (POAK) and LBNL after 3 months of use, and are listed in Table 1. Filter cake was extracted by sonication using a 40:40:20 hexanes/acetone/DCM mixture. Extracts were subsequently filtered through Teflon filters (Millipore FHUP 0047, 2µm) to remove solid residuals. An aliquot was used for direct chromatographic analysis. Filtrates were analyzed using gas chromatography-ion trap tandem mass spectroscopy (GC-IT-MS/MS, Varian 4000). Analytes extracted from filter cake were identified with authentic standards, or tentatively with the NIST library. Total carbon in filter cake was obtained using thermographic methods described by Hadley et al. (2008). FTIR spectra of filter cake were collected using an Attenuated Total Reflection (ATR) cell in a Nicolet 760 spectrometer.

Sampling Location	Type	Material and Media Coating	MERV number	Thickness
unused	Panel	Fiberglass, heavy application of tackifier	6	2"
POAK				
LBNL				
unused	Roll	Polyester, medium application of tackifier	5	1"
POAK				
LBNL				
unused	Pleated panel	Cotton-polyester blend, no tackifier	6	2"
POAK				
LBNL				

Table 1. HVAC filters used in the study.

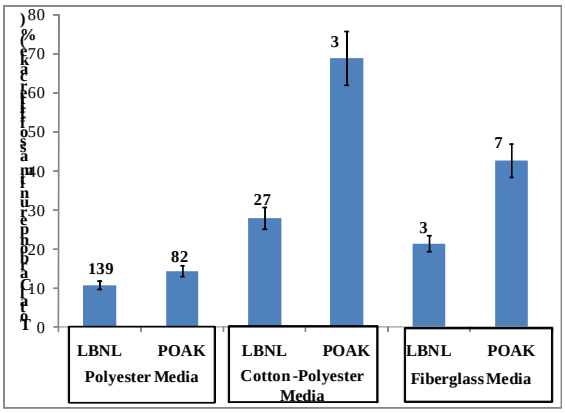
Ozonolysis of α-Terpineol on HVAC filter surface: A Teflon plug-flow reactor designed to hold filter samples perpendicular to airflow was used to study surface ozone reactions of α-terpineol on the HVAC filter (Destaillats and Fisk, 2010). Each filter sample was secured into a filter holder placed inside the reactor. Using a 10 µL or a 100 µL syringe (Hamiliton), the desired

amount of α-terpineol was spiked evenly across the surface of the filter sample. Two levels were studied for all clean filters: 0.54 mg cm^{-2} and 5.4 mg cm^{-2} surface dosage; one concentration, 0.54 mg cm^{-2}, was studied for soiled filters. Ozone level in the upstream of the filter samples was controlled by a UV O_3 generator (UVP Inc., Upland, California) and the upstream concentration levels of ozone were maintained at 150 ppbv for all the experiments. Samples of VOCs, carbonyls, and aerosol particles where collected at the downstream end. The ozone concentration was also monitored and recorded downstream (Teledyne - API 400). All experiments were conducted at 12% RH. Details of sampling methods can be found elsewhere (Destaillats and Fisk, 2010, Sidheswaran et al., 2010)

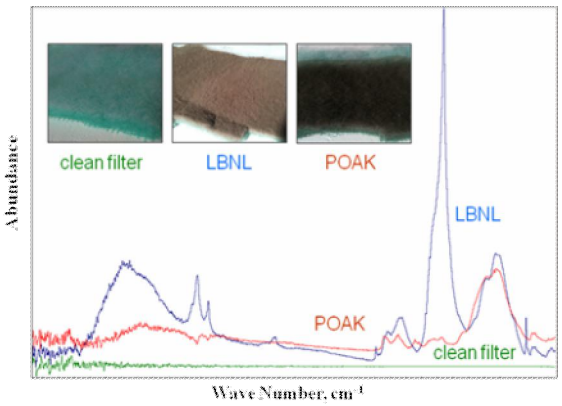
RESULTS

Characterization of filter cake: The chromatographic analysis of the dissolved liquid phase yielded a total of ~100 compounds that were identified, some of which are listed in Table 2. The compounds were broadly classified into six categories based on the possible sources, and the abundance (denoted by the symbol +) was approximately estimated from the peak areas. The organics found included linear alkanes, alkenes, aldehydes, ketones, aromatics, phthalates, sulfur- and nitrogen-substituted organics and carboxylic acids. Zheng et al. (2000) found that solvent extraction of ambient particulate matter from Hong Kong urban air contained 46-80% fatty acids, 10-34% alkanes, 4-21% alkanols and 1-6% PAHs. A semi-quantitative analysis of our filter extraction results also shows a similar pattern, although no PAHs were observed. It should be noted that various compounds observed in these filters have unsaturated double bonds and reactive sites in their molecular structure. This can facilitate ozone reactions on filter surfaces and explain the absence of some reactive species (such as PAHs) present at low levels, compared to the ambient particulate matter. High levels of phytol were observed in LBNL samples, consistent with the prevalence of biogenic sources. Low levels of its oxidation byproduct 2-pentadecanone-6,10,14,trimethyl were also observed in the same filters. It was also found that the organics present in the filters were different at each location. The filters retrieved from LBNL contained more organics of biogenic origin compared to the ones obtained from POAK, which showed pollutants associated with motor vehicle emissions.

Figure 1A shows the total carbon per unit mass of filter cake for the different types of filters. We observed that the total carbon per unit mass was higher for POAK samples compared to the LBNL samples. This is characteristic of the location of POAK where soot and elemental carbon concentrations from vehicular exhaust are high compared to LBNL. The numbers above each data point in Figure 1A indicate the mass of filter cake collected per unit area of filter (mg cm^{-2}). The fiberglass filter media contained a heavy application of tackifier (adhesive) to attract dust, and hence it is possible that the mass of filter cake collected from this type of filter is lower than the mass of filter cake collected from the others. Figure 1B illustrates FTIR spectra of the solvent insoluble fraction of the filter cake obtained from polyester media collected at each location. The differences in spectral signatures of the filter cake collected from two locations are clearly shown in the figure. The LBNL samples shows peaks corresponding to the possible presence of aliphatic hydrocarbons, olefins and aliphatic acids, while some of those features are not observed in the POAK samples. Figure 1B includes also photographs of each of the samples illustrating clearly the different color and texture of filter cake collected in each location on the same filter.



(a)



(b)

Figure 1. (a) Total carbon per unit mass of filter cake for each filter type. The number above each data point is the mass of filter cake per unit area of filter (mg/cm^2) (b) FTIR spectra of solvent insoluble filter cake obtained from polyester filter media (pictures inlay are the polyester media samples showing clean, LBNL and POAK deployed filters)

Analyte	Abundance	Analyte	Abundance
Compounds of Biogenic Origin		***Occupant – Related***	
Phytol	+++	Benzamide N-propyl	++
Oxiraneundecanoic acid, 3-pentyl-, methyl ester, cis-	+	Octadecanoic acid	+
2-Butyloxycarbonyloxy-1,1,10-trimethyl-6,9-epidioxydecalin	+	Dehydropregnenolone acetate	+
Normethadol	+	***Outdoor Urban Pollution***	
1,5-Heptadien-4-one, 3,3,6-trimethyl-, Artemesia	+	2-Dodecanone	++
Ethyl iso-allocholate	+	trans-2,3-Epoxyoctane	+
Olean-18-ene	+	cis-2,3-Epoxyoctane	+
Indoor SVOCs		1-Methylcyclooctanol	+
Phthalic acid, isopropyl propyl ester	++	1-Methylcyclohexanol	+
Phthalic acid, cyclobutyl propyl ester	++	Styrene	+++
1,2-Benzenedicarboxylic acid, monobutyl ester	++	2-methylpropyl-cyclopentane	++
Phthalic acid, hex-2-yn-4-yl propyl ester	++	Benzene, 1,1'-(3-methyl-1-propene-1,3-diyl)bis-	++
1,2-Benzenedicarboxylic acid, butyl octyl ester	++	6-Tetradecanone	++
Benzyl butyl phthalate	+++	Stannane, tetraethyl-	++
Diethylene glycol dibenzoate	++	Ethanol, 2-(4-phenoxyphenoxy)-, benzoate	++
Byproducts of Indoor Chemistry		Octadecanoic acid	+
2-pentadecanone-6,10,14,trimethyl	+	Oxiraneundecanoic acid, 3-pentyl-, methyl ester, cis-	+

Table 2. Compounds tentatively identified in filter cake from LBNL, POAK, and both locations

Ozone - α-Terpineol Reactions on Filter Surfaces: Formation of particulate matter in gas phase reactions of ozone and α-terpineol was not observed when the flow reactor was used in the absence of filter media. However, when filter media was present, we observed particles in the 10-100 nm ultrafine size range. Similarly, gas phase reaction byproducts observed in the presence and absence of filter media were different. In the absence of surfaces, we detected acetone, acetaldehyde, formaldehyde, glyoxal, 1-oxopropanal, 4-methyl-3-cyclohexen-1-one, and 6-hydroxy-hept-5-en-2-one downstream of the reactor. When filter media was present, the main products of α-terpineol ozonolysis were found to be 1,4-butanediol, 4-oxopentanal, 5-(1-hydroxy-1-methylethyl)-2-methylcyclohex-2-en-1-one, 3-(1-hydroxy-1-methylethyl)-6- methyl-cyclohex-2-en-1-one, and 1-(4-methyl-3-cyclohexen-1-yl-)-ethanone. The chromatogram of the volatiles from the ozone - α-terpineol reactions on filter surfaces showed other numerous peaks that were tentatively identified as aromatics substituted with carboxylic groups, nitrogenated compounds, and long chain aliphatic ketones, acids and ethers. These byproducts were location- and material-dependent. For example, undecane cyclohexyl was predominantly produced over cotton – polyester blend filters, while tetrahydrofuran, 2- propyl was found predominantly over fiberglass filters.

Formaldehyde was observed to be produced in the ozone reactions of α-terpineol both on the surface (24 – 10 ppb) and in gas phase (5-10 ppb). Higher concentrations of formaldehyde were observed in all cases compared to the ozone reactions on filters without α-terpineol (1-5 ppb). The formaldehyde concentrations were also found to increase proportionally with the increase in surface dosing of α-terpineol. Similar observations were made for all of the other identified volatile byproducts. The particle number concentration also increased with higher α-terpineol surface dosing. Further, polyester and cotton/polyester media produced more ultrafine particles than fiberglass media in all cases. This is likely due to the different filtration efficiency, according to model predictions by Waring and Siegel (2010). In our samples, efficiency was determined primarily by media thickness, material type and presence of tackifier.

CONCLUSION

The results presented in this study shed light on the importance of HVAC filter cake as a source of primary and secondary indoor pollutants. The chemical characterization of filter cake allowed us to identify some potentially reactive compounds that can react in the presence of oxidants such as ozone. High molecular weight compounds with unknown mass spectra were also observed in chromatograms of the filter cake extracts that may be present in dust particles or originate in filter surface reactions. A more detailed study is warranted to investigate the origin and potential reactivity of those species.

Ozone - α-terpineol reactions conducted on filter surfaces in this study help understand the importance of surface chemistry in HVAC systems. The α-terpineol ozonolysis reactions on the surface of the filters produced ultrafine particulate matter and gas phase species that were not observed when α-terpineol reacted with O_3 in the gas phase. The time averaged total particulate number concentration (in the range 0.4 – 91.4 cm^{-3}) was found to be dependent on the α-terpineol concentration, filter material and filter dust composition.

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